

Detection of petroleum accelerant residues on partially burnt objects in burning/arson offences

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Residues of incendiary materials such as kerosene, petrol (gasoline) or diesel were extracted directly into ether or from the steam distillates of some of the partially burnt objects encountered in cases of burning. The residual petroleum hydrocarbons (aromatics) were converted into their corresponding phenols/naphthols, which were further detected by thin-layer chromatography/high performance thin-layer chromatography by visualizing the plates under UV light before spraying, and in daylight after spraying with diazotized p-nitroaniline reagent followed by aqueous ethanolic sodium hydroxide solution. Though time-consuming, the proposed method is sensitive and would add to the specificity of analysis.

Les résidus de matériaux incendiaires, tels que du Kérozène, de l'essence (gazoline) ou du diesel ont été extraits directement dans l'éther, ou par distillation de vapeurs de certains objets partiellement brûlés, rencontrés dans les cas d'incendie. Les hydrocarbures résiduels du pétrole (aromatiques) étaient convertis dans leur phénols et naphthols correspondants, qui étaient ensuite détectés par chromatographie sur couche mince et chromatographie sur couche mince à haute performance en révélant les plaques sous une lumière UV avant de les traiter et en lumière du jour après traitement avec un réactif de p-nitroaniline diazotisée suivie d'une solution aqueuse éthanolique d'hydroxyde de soude. Bien que longue, la méthode proposée est sensible et permettrait d'augmenter la spécificité de l'analyse.

Von teilweise brandbetroffenen Gegenständen wurden die Rückstände von Brandlegungsmitteln, wie Kerosin, Benzin oder Diesel unmittelbar in Äther oder mittelbar aus dem Dampfdestillat extrahiert. Die öligen Kohlenwasserstoffrückstände wurden anschließend in ihre Phenole und Naphthole umgewandelt und mittels TLC und HPTLC untersucht. Die Auswertung der Platten erfolgte unter UV-Licht und nach Behandlung mit diazotiertem p-Nitroanilin sowie alkoholischer Natriumhydroxidlösung auch unter Beleuchtung mit Tageslicht. Die Methode ist zwar zeitaufwendig, sie ist aber empfindlich und verbessert die Analysengenauigkeit.

Se extrajeron bien directamente en éter o bien por destilación con vapor, los residuos de materiales incendiarios como queroseno, gasolina, o diesel, de algunos objetos parcialmente quemados encontrados en casos de incendios. Los hidrocarburos residuales del petróleo (aromáticos), se convirtieron en sus correspondientes fenoles/naftoles que fueron posteriormente detectados por cromatografía de capa fina/cromatografía de capa fina de alta resolución, visualizando las placas bajo luz ultravioleta antes de revelarlas y a la luz solar tras el revelado con el reactivo de p-nitroanilina diazotado seguido de solución acuosa de hidróxido sódico metanólico. Aunque lleva tiempo, es un método que tiene sensibilidad y añade especificidad al análisis.

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Introduction

Fire accelerants including kerosene, petrol (motor gasoline), and diesel, are often encountered in arson cases and, in countries such as India, these may include cases of homicidal or suicidal burning, connected with "bride burning" in dowry disputes. Kerosene, being readily available as a subsidized domestic cooking fuel, is often misused as a fire accelerant in such cases. Diesel is also used as a cooking fuel and is therefore sometimes involved.

Detection of these accelerants is thus of vital importance legally, and partially burnt exhibits including clothes, cloth materials and skin, recovered from the body of the victim, the accused and the scene of the crime, may be referred to forensic science laboratories for the detection and characterization of the petroleum residues. Accelerants leave residues which are relatively non-volatile and have little smell, and this makes it difficult to detect the parent accelerant among the solid hydrocarbon residues left after an incident. Methods for their detection and characterization have long been a subject of forensic interest.

Many physico-chemical methods have been used for the detection and identification of fire accelerants [1–8], with varying degrees of success. However, all these methods can be expensive, and some do not give enough information to draw definite conclusions. The present work describes the development of simple, inexpensive, selective and sensitive thin-layer chromatography/high performance thin-layer chromatography (TLC/HPTLC) methods. These enabled the detection of aromatic hydrocarbons such as naphthalene and alkyl naphthalenes, present in the solid residues of kerosene, petrol and diesel [1, 5, 8] in burning cases, by their conversion into the corresponding phenols and naphthols, and further detection by diazotization and coupling.

Experimental

Different kerosene samples were bought from the market, and samples of petrol and diesel were obtained from various petroleum companies. These were used to prepare control (reference) samples on 15 cm x 15 cm pieces of cotton, synthetic (nylon) and terry towelling cloth.

Ethyl alcohol (95% v/v, re-distilled) and moisture-free diethyl ether were used, and all reagents and

chemicals were of analytical grade. Standard thin-layer chromatographic equipment, Silica Gel-G, HPTLC (CAMAG, NANO, MAT II) equipment, HPTLC glass plates coated with silica gel-60F-254, microlitre pipettes, an air blower and a quick-fit assembly for distillation, and a Shimadzu-160A-UV-visible spectrophotometer were all used in support of this research.

Sample preparation

Small pieces of partially burnt/charred exhibits received in case work, including samples of clothes, bed linen, pillows, mattress, carpet, skin, papers, coal and hay, were extracted with 3×10 ml portions of ether. The combined ether extract was filtered and evaporated at room temperature to produce a small volume of about 0.5 ml for phenol/naphthol derivatization. Dirty or half-burnt exhibits, for which a colourless ether extract could not be achieved, were subjected to steam distillation. Pieces of the exhibit were placed in a quickfit distillation flask with distilled water and steam distilled until about 15–20 ml of distillate were collected. This distillate was extracted with 3×10 ml of ether and the combined extract was evaporated to a volume of 0.5 ml as above.

Control samples of common accelerants were prepared by soaking pieces of cloth (15 cm x 15 cm) with 0.02 to 0.4 ml of kerosene, petrol or diesel (applied dropwise as 0.02 ml aliquots, using a graduated pipette). Samples were also prepared using 2 ml of commonly used vegetable oils such as groundnut, coconut, and palm oils, and about 2 ml of human body fat, recovered from biological materials. Some pieces of cloth were also stained with about 500 mg of road tar. Blank pieces of cloth acted as negative controls. All pieces of cloth were then set alight and partially burnt, simulating the samples received in actual casework, and extracted directly with ether, filtered and concentrated into a small volume (about 0.5 ml) before derivatization.

Phenol/naphthol derivatization

Each concentrated ether extract (about 0.5 ml) was transferred to a 20 ml test tube, mixed with 0.5 ml concentrated sulphuric acid and heated in an oil bath, maintained at $160^{\circ}\text{C} \pm 1^{\circ}\text{C}$ for 3 minutes, with intermittent shaking. It was then cooled to room temperature, mixed with 1.0 ml of saturated (or 20%

w/v) solution of sodium chloride, and again heated with shaking for 1–3 minutes in an oil bath.

A mixture of 0.5 ml of water and 8–10 pellets of potassium hydroxide was heated in a silica crucible on a burner without the wire gauze, until the pellets were completely dissolved. The contents of the test tube were then poured into the crucible and stirred, and the mixture was carefully heated on the burner, avoiding spurting or charring of the contents. When the contents had evaporated to dryness, the crucible was allowed to cool to room temperature and the contents were dissolved in 5 ml of distilled water and slowly acidified with concentrated hydrochloric acid. The acidified solution was then extracted with ether and the extract was concentrated to about 0.5 ml for use in the TLC/HPTLC studies.

Thin layer chromatography

Two spray reagents [9] were prepared. Freshly prepared 0.3% w/v solution of p-nitroaniline in 8% v/v hydrochloric acid (25 ml) was mixed with 1.5 ml of 5% w/v solution of sodium nitrite in water. The second reagent was a 10% w/v solution of sodium hydroxide in ethanol:water (1:1).

Solutions (0.01% w/v) of β -naphthol, 4-methyl-1-naphthol and 3,4-dimethyl-1-naphthol were prepared in diethyl ether to act as reference marker samples.

TLC plates were prepared on standard 20 cm \times 20 cm glass plates coated with about 25 mm thick silica gel-G layers activated at 110°C for 1 hour in a hot air oven. Suitably concentrated ether extracts (20 μ l) from the analyte solutions derived from case samples, controls and negative controls were spotted onto the TLC plates, with reference marker solutions. The plates were developed in a previously saturated (about 1 hr) chamber with a solvent system of chloroform:xylene (3:1) up to a length of 12 cms from baseline. The plates were dried at room temperature with an air blower and sprayed with the diazotized p-nitroaniline followed by aqueous-ethanolic sodium hydroxide. The developed chromatogram was observed in daylight.

In an attempt to identify the major individual constituents of these residues, the spots from control derivatized petrol, kerosene, and diesel residues corresponding to the R_f of the reference markers β -naphthol, methyl naphthol and dimethyl naphthol (0.43, 0.30 and 0.21 respectively) were separately eluted from the plate in ethanol before spraying. The UV-absorption spectra of each filtered eluate was recorded over the range 200 to 400 nm range.

Similarly UV spectra of the reference markers of the various naphthols in ethanol were also recorded separately for comparison.

High performance thin-layer chromatography

The same solutions were also spotted on to HPTLC glass plates, precoated with silica gel-60-60F-254. The chromatograms were then developed and observed as described above.

A number of other chromogenic reagents used for the detection of phenols, naphthols and alkyl naphthols were tested as spray reagents. These included a mixture of 0.5% w/v sulphanilic acid in 2% w/v hydrochloric acid and 0.5% w/v sodium nitrite followed by 10% w/v sodium bicarbonate solution; 1% w/v 5-nitroso- β -hydroxyquinoline in concentrated sulphuric acid; freshly prepared 5% w/v aqueous solution of sodium cobaltinitrite and dilute acetic acid; 1% w/v solution of sodium nitrite in sulphuric acid.

Results and discussion

When TLC/HPTLC plates were observed under UV light at 366 nm before spraying, a characteristic pattern of well separated violet fluorescent spots was seen for each of the derivatized residues of kerosene, petrol, diesel and bituminous tar. When the plates were sprayed with the chromogenic reagents, a pattern of well separated, brilliant, intense reddish orange/pinkish brown spots was revealed for each residue (Figures 1a and 1b). The petroleum products could thus be easily differentiated with respect to the total number of spots, their shape, colour, position and relative distribution. Unknown case samples could be identified by comparing their TLC/HPTLC chromatographic patterns with those of the known control samples. When alternative spray reagents were tested, all gave an equally good response. Hence, any one of them could be used for this technique.

The UV-absorption spectra of the solutions from the eluted TLC spots of the petroleum residues showed the same characteristic patterns and λ_{\max} values as those of the standard reference markers β -naphthol, 4-methyl-1-naphthol and 3,4-dimethyl-1-naphthol when compared experimentally and from their reported values [10]. These UV spectral results further support the TLC results of the naphthol derivatization, and both studies together indicate the presence of naphthalene, methyl-naphthalene and dimethyl naphthalene as prominent parent aromatic hydrocarbons in the petrol, kerosene and diesel

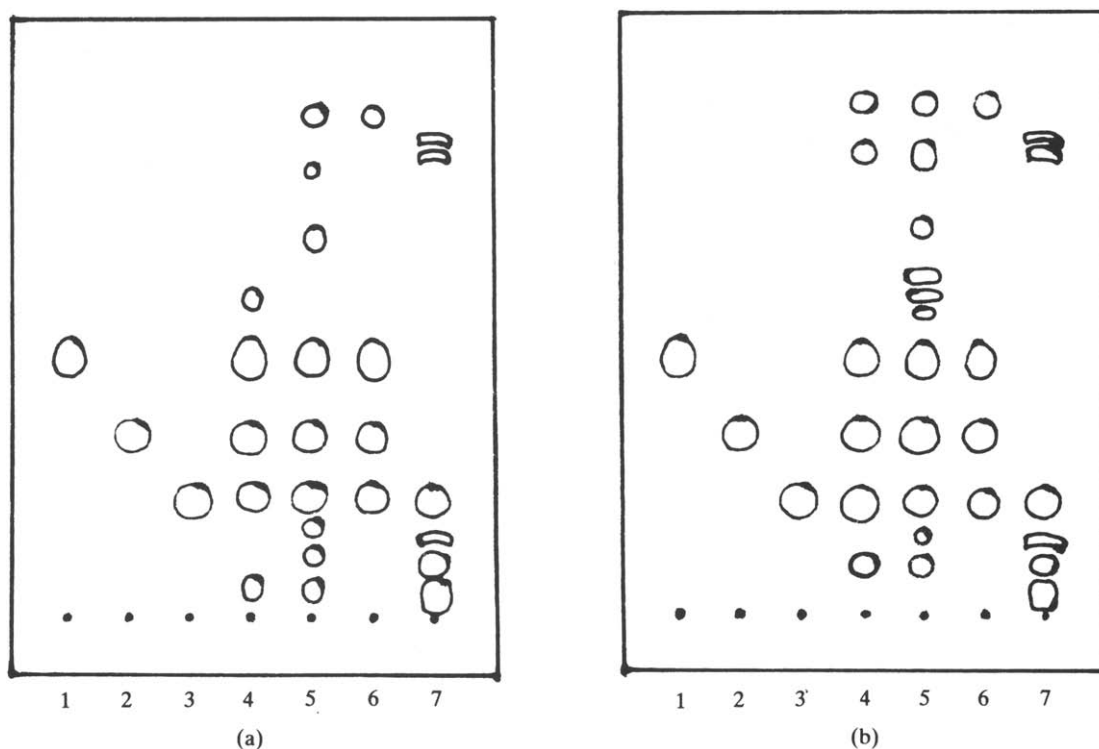


FIGURE 1 TLC chromatogram (a) and HPTLC chromatogram (b) of reference markers β -naphthol (1), 4-methyl-1-naphthol (2) and 3,4-dimethyl-1-naphthol (3), and control samples of derivatized residues of kerosene (4), diesel (5), petrol (6) and bituminous tar (7).

residues. Other spots (Figures 1a and 1b) from derivatized petrol/kerosene diesel residues could not be individually identified further for the want of other branched alkyl substituted naphthols, as control reference markers. The control negative blanks, vegetable oils and human body fats showed no spots after spraying.

Conclusions

Several workers have established that naphthalenes are present in high concentrations in the residues of kerosene, petrol and diesel in partly burnt samples [1, 5, 8, 11]. The procedure described above utilizes derivatization and successfully converts the parent hydrocarbons into their corresponding phenols and naphthols as a means of identification. Although more time-consuming, the method is more sensitive and selective than earlier TLC methods which do not employ derivatization [2–4, 12] and amounts as little as 0.04 ml of kerosene and diesel, and 0.2 ml of petrol could be detected. Tar and bituminous stains also present in charred samples could be differentiated by this method from other commonly-used petroleum products, and impurities such as vegetable oils and body fats did not interfere.

Thus the method could prove to be useful in forensic science laboratories in routine cases involving kerosene, petrol and diesel residues as a complementary analytical method alongside routine GC-FID studies. It could also be used as a simple screening procedure prior to NMR or GC-MS analysis in the more sophisticated laboratories. At the same time, however, we acknowledge that much work remains to be done in this area before the relationship between various accelerants, substrate materials and the effects of fire and pyrolysis on them is understood.

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